A 140 GHz prepolarizer for dissolution dynamic nuclear polarization

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Apart from their very classical use to build polarized targets for particle physics, the methods of dynamic nuclear polarization (DNP) have more recently found application for sensitivity enhancement in high-resolution NMR, both in the solid and in the liquid state. It is often thought that the possible signal enhancement in such applications deteriorates when the DNP is performed at higher fields. We show that for a dissolution-DNP method that uses conventional (2,2,6,6-tetramethylpiperidine 1-oxyl) radicals as the paramagnetic agent, this is not the case for fields up to 5 T. © 2008 American Institute of Physics. [DOI: 10.1063/1.2951994]

I. INTRODUCTION

Dynamic nuclear polarization (DNP), in the sense of the present paper, is the enhancement of nuclear spin polarization in a solid by transfer of polarization from the electron spins of paramagnetic centers that are fixed with respect to the nuclei. Its typical application is in particle physics, where it is used to polarize nuclei in a “polarized target,” usually consisting of glassy (frozen) beads of alcohol/water mixtures.¹

The application of DNP to liquid-state NMR (Refs. 2 and 3) (“dissolution DNP”) is based on the transformation of a frozen-bead sample into a polarized liquid room temperature solution by rapid dissolution in superheated water. For solid-state NMR, methods have been developed that combine DNP and ¹³C magic angle spinning (MAS) NMR.^{4–7} An important technical difference between the solid- and the liquid-NMR technique is that in the first case the DNP and the NMR observation are conveniently done in the same magnetic field, whereas in the second case separate magnets can easily be used. For reasons of NMR resolution, the magnetic fields in MAS-NMR are at least 5 T [140 GHz electron spin resonance (ESR) frequency].⁷ The original development of dissolution-DNP (Ref. 3) used 3.35 T (94 GHz), as does all now commercially available equipment.

No dissolution-DNP prepolarizer at higher frequency has been described so far, perhaps because of the increasing cost of microwave power. Another reason may be that the signal enhancement (at least in MAS-DNP) can decrease when the field increases.⁷ While in MAS-DNP the advantage of increased resolution can offset this disadvantage in sensitivity, there is no such argument for dissolution DNP, where the polarization and observation fields are always independent.

In this paper we present the first results obtained at 140 GHz after a minimal modification of our prepolarizer.⁸ The efficient microwave coupling structure of that design allows us to obtain the gain in polarization expected from the

Borghini model,⁹ using only 30 mW power at the output of the microwave source. The hardware and the method of the dissolution step⁸ remain the same, so the increased polarization should also be available after the dissolution.

II. THE BORGHINI MODEL

Many, often subtly different, mechanisms for the DNP effect have been proposed in the literature. A very pedagogical discussion is in an early paper¹⁰ that unfortunately is not easily available. A good recent summary can be found in Ref. 7. At the relatively high temperatures at which MAS experiments are performed, there are indications^{5,7,11} that the enhancement of nuclear polarization is inversely proportional to the magnetic field (in that case the value of the enhanced polarization becomes field independent); but polarized-target experiments at temperatures well below 1 K also mention a decrease in polarization upon increasing field (see Fig. 7 in Ref. 12 and Fig. 1 in Ref. 13). On the other hand older data on deuterons taken at 2.5 and 5 T fields and a temperature of 1.05 K (Refs. 14 and 15) rather seem to point to an opposite effect. Therefore it is not yet clear what can be expected for the field dependence of dissolution DNP.

The results that we present in this paper can be qualitatively understood from a rather simple spin temperature theory for inhomogeneous ESR lines.⁹ In its basic form this Borghini model has no adjustable parameters. It is an extension of Redfield's¹⁶ model of a single spin temperature in the rotating frame. It does not require the high-temperature approximation (equivalent to Curie's law) for the electron spin magnetization, contrary to the Provotorov theory with two spin temperatures.¹⁷

Consider the ESR spectrum of a glassy sample containing radicals with *g*-anisotropy only. That spectrum is a superposition of resonances from radicals with distinct orientations of the applied field **B** with respect to the principal axes of their *g* tensors. In a glass, these orientations should be uncorrelated even between nearest neighbors, by analogy with the ¹³C chemical shift tensors in simple methanol

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glasses.¹⁸ For spin temperature theory this implies that in the ESR spectrum there can be strong dipolar couplings between spins that are spectrally far apart, contrary to the case of a powder. Qualitatively, this should help the mechanism of spectral diffusion to establish a spin temperature across the inhomogeneous line, a fundamental condition of the Borghini model.

Let the ESR lineshape function $f(\Delta)$ and the relative frequency scale Δ be normalized as

$$\int_{-\infty}^{\infty} f(\Delta) d\Delta = 1, \quad \int_{-\infty}^{\infty} \Delta f(\Delta) d\Delta = 0 \quad (1)$$

and let the absolute frequency in the point $\Delta=0$ be ω_0 . The microwave field has frequency ω , which corresponds to an offset Δ_0 with respect to ω_0 . In the spirit of the Redfield approach, we transform to a frame rotating at ω . The effective Zeeman field in this frame is composed of the offset field $(\Delta_0 - \Delta)/\gamma_e$ along the z axis and the microwave field ω_1/γ_e along the x axis. The Borghini hypothesis⁹ is that electron dipole-dipole interactions are strong enough to establish a uniform spin temperature in the rotating frame, but that their contribution to the spin energy in that frame can be neglected. Furthermore, the contribution of the microwave field to the Zeeman energy in the rotating frame is neglected, as is usually done in Redfield theory. Let $\beta = \hbar/kT$ be the inverse spin temperature parameter in the rotating frame and $\beta_L = \hbar/kT_L$ the inverse lattice temperature. With the above approximations, the conservation of energy in the rotating frame says that β , as function of $\beta_L\omega_0$ and Δ_0 , is given by the solution of

$$\tanh\left(\frac{1}{2}\beta_L\omega_0\right) = \int_{-\infty}^{\infty} f(\Delta) \tanh\left(\frac{1}{2}\beta(\Delta_0 - \Delta)\right) \frac{\Delta_0 - \Delta}{\Delta_0} d\Delta. \quad (2)$$

For a detailed derivation of this result see Eq. (6.102) in Ref. 19. The β derived so far is the inverse electron spin temperature in the electron rotating frame. Now a further hypothesis is that thermal mixing transmits this same inverse temperature to the nuclear spins in the laboratory frame.

At low lattice temperature and for typical inhomogeneous linewidths in 2.5–5 T fields, numerical solutions of Eq. (2) predict that the maximum inverse spin temperature $\beta_{\max}(\Delta_{0,\text{opt}}, \beta_L\omega_0)$ is independent of the field. The model does not consider time constants, and does not say whether at this “best” microwave offset $\Delta_{0,\text{opt}}$ the value $\beta_{\max}$ can be obtained in any practical time. Only one extensive analysis of experimental DNP data using this model has been published so far.¹² While the above parameterless version of the Borghini model gave a qualitative understanding of the variation of $\beta_{\max}$ with field and temperature, quantitative agreement was only obtained after including the nuclear spin-lattice relaxation.¹² This introduces a parameter usually called the leakage factor.

In the process that we considered so far, the nuclear spin temperature in the laboratory frame simply relaxes toward the electron spin temperature in the rotating frame. Leakage adds the competition of relaxation of the nuclear spin temperature toward the lattice temperature. This process can be

FIG. 1. Results at 94 GHz. (a) Calculated TEMPO ESR spectrum. (b) Calculated ^{13}C microwave spectrum. (c) Experimental ^{13}C microwave spectrum. (d) Polarization time constants across the microwave spectrum.

seen as an additional heat load on the electron spin system, that equilibrates β at lower values than the $\beta_{\max}$ calculated from Eq. (2); at the same time there is a shift of $\Delta_{0,\text{opt}}$. Similar effects (higher β , smaller $|\Delta_{0,\text{opt}}|$) are found when the lattice temperature increases, from Eq. (2) as well as in experiments.¹² A further consequence of the leakage is that the maximum enhancement $\beta_{\max}$ no longer depends just on the product $\beta_L\omega_0$, but separately on the temperature and the field, since the nuclear spin-lattice relaxation rate has separate dependences on these two factors. In the present paper we will restrict ourselves to a qualitative discussion, using the parameterless Eq. (2).

III. RESULTS AND DISCUSSION

The 140 GHz prepolarizer is identical to the 94 GHz machine that we have described earlier,⁸ except for the microwave source and its connection to the top of the microwave insert, which is a rectangular WR06 waveguide, instead of WR10 on 94 GHz sources. The bottom part of the

FIG. 2. Results at 140 GHz. (a) Calculated TEMPO ESR spectrum. (b) Calculated ^{13}C microwave spectrum. (c) Experimental ^{13}C microwave spectrum. (d) Polarization time constants across the microwave spectrum.

microwave insert and all other cryostat inserts remain the same. We use the same type of superconducting magnet, but now set it to 5 T instead of 3.35 T. The 140 GHz microwave source (Elva-1, type VCOM-06/140) can be tuned over ± 0.5 GHz, and has a lower output power, but is otherwise similar in design to the 94 GHz sources used on most commercial prepolarizers.

We illustrate the relative performance of our two machines on the example of ^{13}C enhancement in our typical sample: $3M$ ^{13}C -labeled acetate in a deuterated solvent, 67/33 water/ethanol with about 50 mM of 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) radical. Although this composition does not yield the very best performance,²⁰ we have found such samples to be extremely reproducible and stable,^{8,20} and therefore very suitable for comparative measurements.

Figures 1 and 2 give results at 94, respectively, 140 GHz. The top panel in each figure shows the theoretical ESR spectrum of TEMPO, calculated using the package EASYPIN (Ref. 21) with parameters taken from Ref. 22. The

FIG. 3. Effect of microwave power level at 140 GHz. (a) Stationary ^{13}C polarization. (b) Temperature in the bath.

second panel gives the microwave spectrum (nuclear polarization in the stationary state as a function of irradiation frequency) for ^{13}C according to Eq. (2). The third panel shows the corresponding experimental result. The bottom panel shows the polarization time constant for the ^{13}C nuclear polarization (the exponential time constant for the growth of the polarization from the moment that the microwaves are switched on). Figure 3 shows how at 140 GHz the final polarization and the temperature measured by a thermometer in the bath vary with microwave power (measured at the input to the microwave insert).

The overall features of the experimental microwave spectra, in particular the increase in asymmetry at 140 GHz, are reproduced by the Borghini model, but the experimental spectra are narrower and have smaller amplitudes than the theoretical ones. These differences can be ascribed to leakage. In particular the lower amplitudes are similar to those found in Ref. 12. That the spectra are narrower can be understood from the lower panels in Figs. 1 and 2 that show how far out in the wings the polarization times become extremely long, and that therefore relaxation effects (not accounted for in the parameter-free version of the Borghini model) will reduce the actual polarization to nearly zero. The ratio of the best polarizations at 140 and 94 GHz (1.35 for positive and 1.85 for negative polarization) is of the order 140/94; the calculated microwave spectra have a similar asymmetry in the ratios. We have found comparable results for a sample of $1.5M$ ^{13}C -labeled glycine in a deuterated 40/60 water/glycerol solvent with 50 mM TEMPO, and for a $2.5M$ solution of labeled Na-pyruvate salt in a deuterated 82/18 water/ethanol solvent with 33 mM TEMPO.

The data in Fig. 3 require little comment. It is seen that the optimal polarization can be obtained with less than the guaranteed output power (55 mW) of the microwave source, and that the cooling power of the cryostat remains adequate. These results are very similar to those at 94 GHz.⁸

IV. CONCLUSIONS

We have shown elsewhere²⁰ that, as expected for our kind of samples, the DNP mechanism is thermal mixing. The

qualitative agreement between the predictions of the (parameterless) Borghini model and experiment shows that the first step in the process is dynamic cooling of the electron Zeeman temperature in the rotating frame. The second step, which is not known in detail, involves the thermal mixing proper: The equalization of the electron spin temperature in the rotating frame and the nuclear spin temperature in the laboratory frame.

For this overall mechanism, the attainable polarization for low- γ nuclei goes as B_0/T_L in the region of practical values of field B_0 and sample temperature T_L . Therefore, for dissolution DNP based on radicals with strongly inhomogeneous ESR lines, such as TEMPO, an operating field of 5 T will typically yield a 50% increase in polarization over the present standard value 3.35 T. From a practical point of view, the incremental cost of the instrumentation is rather modest if the required microwave power remains, as in our case, below 50 mW and if the magnet used can provide the higher field.

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